STUDIES OF WATER-IN-OIL EMULSIONS:
THE ROLE OF ASPHALTENES AND RESINS

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Abstract

This paper summarizes studies to determine the role of asphaltenes and resins in water-in-oil emulsions. Literature shows that asphaltenes are largely responsible for emulsion formation and stability. Recent studies also indicate that resins play an ancillary role in this factor. Furthermore, it has been shown that stability of emulsions can increase with time. This increased stability is attributed to the continued migration of asphaltenes and resins to the oil-water interface. This migration is examined experimentally in this paper.

The stability of emulsions has been studied by examining the asphaltene content and secondarily, the resin content. Results are reported which show that asphaltenes migrate to the oil-water interface over a period lasting as long as three months.

Introduction

The most important characteristic of a water-in-oil emulsion is its "stability". The reason for this importance is that one must first characterize an emulsion as stable (or unstable) before one can characterize the properties. Properties change very significantly for each type of emulsion. The 'stability' of an emulsion itself might be a question. Historically, emulsions were thought of as inherently unstable, therefore any discussion of 'stability' would be considered trivial. This has changed in recent years. Many commercial products resembling water-in-oil emulsions made from crude oil, have been shown to be stable, especially as this relates to their production, sale, storage and use as consumer products.

It has been noted that the stability of emulsions can be grouped into three categories: stable, unstable and meso-stable. These have been distinguished by physical properties. The viscosity of a stable emulsion at a shear rate of one reciprocal second, is at least three orders-of-magnitude greater than that of the starting oil. An unstable emulsion usually has a viscosity no more than two orders-of-magnitude greater than that of the starting oil. The zero-shear-rate viscosity is at least six orders-of-magnitude greater than the starting oil for a stable emulsion. For an unstable emulsion, it is usually less than two or three orders-of-magnitude greater than the viscosity of the starting oil. A stable emulsion has a significant elasticity, whereas an unstable emulsion does not. These properties can then be used in the design of any emulsion-breaking test as a quick analytical tool. It should be noted

that very few emulsions have questionable stability. The usual situation is that emulsions are obviously either stable or unstable. Analytical techniques are then largely required to test the few questionable emulsions or to rapidly confirm the stability of the others.

Studies in the past two years have shown that a class of 'very stable' emulsions exists, characterized by their persistence over several months. These stable emulsions actually undergo an increase in viscosity over time. Monitoring of these emulsions has been performed for over two weeks and new studies over much longer times are being conducted. 'Unstable' emulsions do not show this viscosity increase and their viscosity is less than two orders-of-magnitude greater than the starting oil. The viscosity increase for stable emulsions is at least three orders-of-magnitude greater than the starting oil. The present authors have studied emulsions for many years (Bobra, 1992; Fingas, Fieldhouse et al., 1993a, 1993b, 1993c, 1994a, 1994b, 1995a, 1995b). The last of these references describes studies to define stability. The findings of this study are summarized here. It was concluded both on the basis of the literature and experimental evidence above, that certain emulsions can be classed as stable. Some (if not all or many) stable emulsions increase in viscosity after time. The stability derives from the strong visco-elastic interface caused by asphaltenes, perhaps along with resins. Increasing viscosity may be caused by increasing alignment of asphaltenes at the oil-water interface.

Meso-stable emulsions are emulsions that have properties between stable and unstable emulsions (really oil/water mixtures) (Fingas et al., 1995b). It is suspected that these emulsions lack sufficient asphaltenes to render them completely stable or still contain too many de-stabilizing materials such as smaller aromatics. The viscosity of the oil may be high enough to stabilize some water droplets for a period of time. Meso-stable emulsions may degrade to form layers of oil and stable emulsions. Meso-stable emulsions can be red in appearance or black. Meso-stable emulsions are probably the most commonly-formed emulsions in the field.

Unstable emulsions are those that decompose (largely) to water and oil rapidly after mixing, generally within a few hours. Some water may be retained by the oil, especially if the oil is viscous.

The most important measurements taken on emulsions are creep and recovery rheometry studies. The presence of elasticity clearly defines whether or not a stable emulsion has been formed. The viscosity by itself can be an indicator (not necessarily conclusive, unless one is fully certain of the starting oil viscosity) of the stability of the emulsion. Colour is not a reliable indicator. This laboratory's experience is that all stable emulsions were reddish. Some meso-emulsions also had a reddish colour and unstable emulsions were always the colour of the starting oil. Water content is not an indicator of stability and is error-prone because of 'excess' water that may be present.

The purpose of the present paper is to move the emulsion studies onwards to focus on the classes of compounds responsible for their formation; asphaltenes and resins, and particularly on the migration of these compounds from an oil solution to the oil-water interface.

Literature Review

A literature search was performed specifically of topics that related to the

stability of water-in-oil emulsions and the role of asphaltenes and resins in this.

Neuman and Paczynska-Lahme (1981, 1988) reviewed the properties of crude oil emulsions noting that the emulsions are often very stable. They pointed out that the emulsions are stabilized by the surfactant effects of asphaltenes and resins. Stability is associated with unusually high viscosities - higher than predicted by viscosity equations such as the Einstein equation.

Desmarquest and co-workers (1984) studied the stability of water-in-oil emulsions formed from weathered Arabian crude oil using an interfacial viscosity apparatus. They found that the interfacial viscosity increases with time and this was attributed to the increasing aggregation of asphaltenes.

Eley, Hey and Symonds (1988) studied emulsions using crude oil and crude oil surrogates. Stability was determined by phase separation observation, but also correlated to droplet size distributions, which were found to follow log-normal distributions, and to interfacial area, which is calculated from the volume of water uptake in a given amount of time. The most stable emulsions were found to be formed from oils where the aliphatic/aromatic ratio is such that the asphaltenes are at the point of precipitation.

Paczynska-Lahme (1990) examined oil and emulsions and proposed that water-in-oil emulsions are stable because of the elastic interfacial films formed by the resins and asphaltenes. It was also noted that multiple types of emulsions could apparently coexist in petroleum.

Sjöblom and co-workers (1990a, 1990b) studied several crude oils from Norway and measured emulsion stability by examining phase separation. Asphaltenes were removed and it was found that no oils would produce stable emulsions. The asphaltenic and resinic fraction was analyzed by FTIR and palmitic acid was identified. Addition of the asphaltenes and resins back to oils rendered stable emulsions.

Brandvik and Daling (1991, also Daling and Brandvik, 1988) studied the stability of several Norwegian crude oil emulsions by measuring the water settled out after 24 hours. Stability was assigned a numerical value of one less the fraction of water lost after the 24-hour settling period. Stability correlated most with the viscosity of the oil, then the amount of resins and then the amount of asphaltenes in the oil.

Nordli, Sjöblom et al. (1991) separated interfacially-active components in six different North Sea oils and measured their film properties. The fractions form monomolecular films at the air/water interface and were relatively stable, but could be fractured with surface pressures between 10 and 29 mNm^{-1}. Aromatic solvents were found to interact strongly with the film and modify film properties. The interfacially-active components were asphaltenes and resins and are attributed to be the cause of emulsion stability. The researchers proposed the strength of the surface film they measured is responsible for water-in-oil emulsion stability.

McMahon (1992) studied emulsion stability by observing phase separation or by measuring residual water in the oil phase by Karl-Fischer titration. The hypothesis that wax content influences stability was tested. It was found that the wax influence on stability was present, but not as strong as the asphaltene and resin influence and that the wax influence may not be through action at the interface. It was proposed that the wax influence on stability was exerted by inhibiting film thinning between

approaching droplets.

Mingyuan, Christy and Sjøblom (1992) studied emulsion stability as it related to asphaltene and resin content. The authors concluded that asphaltenes yielded more stable emulsions than resins. They also noted that water-in-oil emulsion stability is a function of aromaticity, polarity, molecular size, and type of functionality in the stabilizing fraction (asphaltenes and resins).

Sjöblom, Urdahl and co-workers (1992a, 1992b) studied the stability of Norwegian oil emulsions and concluded that stability is the result of the asphaltene/resin fraction. Dielectric spectroscopy was also thought to be a useful means of studying stability in addition to phase separation. The interfacial pressure of asphaltenic- and resinic-stabilized emulsions was shown to correlate with stability.

Urdahl, Brekke and Sjöblom (1992) studied the silica-absorbed fractions of crude oil (traditionally taken as resins and asphaltenes) and found that the bulk of the stabilizing fraction consisted of long, straight-chain aliphatic compounds containing a heteroatom substituent.

Acevedo, Escobar and co-workers (1993) studied water-in-oil emulsions by adding and subtracting resins and asphaltenes. It was found that a high viscoelasticity was attributed to the presence of asphaltenes and was correlated with the stability of the emulsion. They also found that resins by themselves would not stabilize the emulsions, but contributed to a high stability of the emulsions. In the absence of resins, asphaltenes were not dispersed and the emulsions less stable. The stability and viscoelasticity were highest in the presence of salt water.

Mohammed, Bailey and co-workers (1993a, 1993b, 1994a, 1994b) studied several aspects of water-in-oil emulsion stability. A rheological study using free oscillation and creep models showed a strong correlation of elasticity with stability. One study also showed that the viscous interfacial films formed between crude oil and water became more elastic and viscous with time, thus increasing the emulsion stability further. In another study, a Langmuir trough was used to study the surface pressure versus area (interfacial tension curves) of resin and asphaltene mixtures. These studies indicate that strong films (and hence stable emulsions) are a result of the flocculation of asphaltene-resin micelles at the interface. In the absence of resins, the asphaltenes behaved differently and were not dispersed but precipitated and formed multiple layers. This could produce a less stable emulsion. All the studies pointed out that the interfacial film ages and becomes stronger and thus the emulsion becomes more stable with time. This is also evidenced in an increasing difficulty breaking the emulsion.

Chaala, Benallai and Hachelef (1994) studied the stability of crude oils with varying asphaltene and wax components. This group has developed a method of rating emulsion stability based on the difference in optical densities of samples, before and after centrifuging. Emulsions are rated on a stability basis of zero to one based on the ratio of the optical density. Studies showed that emulsion stability is decreased by increasing quantities of waxes and aromatics.

Rønningsen, Sjöblom and Mingyuan (1995); and Sjöblom, Mingyuan and co-workers (1995) studied the effects of the exposure of crude oils to air and light. The crude oil changed as a result of this exposure and was generally able to form water-in-oil emulsions more readily as a result of this. This was attributed to the formation of various oxidation products, mainly carbonyl compounds (resins). The water-in-oil

emulsions became more stable with increasing exposure. However, in a limited number of cases this was not the case indicating that not all compounds with a high interfacial activity were supportive of water-in-oil emulsion stability.

Schildberg, Sjöblom and co-workers (1995) studied resins and asphaltenes in crude oils by extracting them and characterizing them with FT-IR, chromatography, interfacial properties and interfacial tensions. The resin and asphaltene fractions were found to be responsible for the stability of water-in-oil emulsions. The definition of what constitutes an asphaltene or resin was found to be diffuse. It was also found that there is interaction between asphaltenes and resins.

Urdahl and Sjöblom (1995) studied emulsions from the Norwegian Continental Shelf. They concluded the indigenous interfacially-active components (asphaltenes and resins) in the crude oil are responsible for stabilization. Model systems stabilized with resins and asphaltenes display properties similar to the natural crude oil emulsions.

Førdedal, H., Y. Schildberg and co-workers (1996) studied crude oil emulsions using time-domain dielectric spectroscopy (TDS). They found that stability in crude oil emulsions could be described and modelled by the amount of separated asphaltene fraction. It was found that the resin fraction was more interfacially active than the asphaltenes, but could not stabilize emulsions by themselves. It was concluded that the interaction between resins and asphaltenes are the critical factor determining emulsion stability.

Experimental

Laboratory Formation Techniques
One of the objectives of the investigation into emulsions is to have a standard method of forming the emulsion from a given oil. Formation methods for two different apparatuses were used. Each uses a different means of supplying energy to the oil/water system, and both are commercially available.

Rotary Agitator
This apparatus imparts energy to the oil/water by an end-over-end rotation of glass cylinders. The apparatus is a standard extraction apparatus specified in an EPA standard, unrelated to oil emulsions.

The procedure is summarized in the following paragraph:

The apparatus is an 8-place Rotary Agitator from Associated Design and is equipped with a variable speed motor from 1.5 to 56 rpm. The mixing vessels are Wheaton 2.2 litre wide mouth glass bottles. The fill is 500 mL salt water (3.3% w/v NaCl) and 20 mL oil. This yields an oil-water-ratio of 1:25. Studies are performed at 50 rpm, which is set using a tachometer. The mixture is rotated for 3 hours. The specific method is as follows: place rubber collars on glass bottles at the midway point. Add 500 mL salt water and 20 mL oil to the mixing vessel. Place Teflon lid liners on the bottles and cap. These steps should be performed as quickly as possible to reduce exposure of the oil. Insert the bottles into the rotary agitator at the rubber collars, such that the cap is leading into the direction of rotation. Rotate at 50 rpm for 3 hours. Remove the bottles and pour off the water. Collect the emulsion in an appropriately sized beaker.

Blender

The method employed in our laboratory is as follows:

The Waring 1 litre Duo Speed Commercial Blender is used with an Eberbach 1 litre borosilicate container with stainless steel blender assembly. The fill is 70 mL salt water (3.3% w/v NaCl), additional 25 mL aliquots as needed and 30 mL oil. The starting oil-to-water ratio is generally 1:4. The mixture is stirred with 15,500 rpm blade rotation. The mixture is agitated for 30-second intervals until a stable (as determined visually) emulsion forms. The specific methodology is as follows: combine 70 mL salt water with 30 mL of oil in the blender vessel. Turn blender on at low setting for 30 seconds. Stir with a rubber policeman and add 25 mL salt water. Turn on blender again for 30 s. Stop, stir and repeat. If an excess of at least 2 mL water is not present, add another 25 mL aliquot of salt water. Continue to blend, stir and add water until an excess of water is obtained. Additional water is not normally required. When emulsion formation is complete, pour off the excess water and pour/scoop the emulsion into an appropriately sized beaker.

Procedures to Study the Migration of Resins and Asphaltenes

Emulsion Formation and One Week Standing

Emulsions were formed using the specified crude oil according to selected standard emulsion formation procedures outlined above. The emulsion was then placed in a large beaker and allowed to stand in a 10 degree cold room for 1 week.

Separating Oil and Emulsion

Free Oil Layer - The oil layer on top was removed using a syringe with a large gauge needle. The oil was collected as close to the surface as possible, with care taken to avoid the emulsion below. This sample was called the "free oil". If the emulsion was semi-solid, the beaker was tipped to concentrate the oil at one end. Remaining oil on top of the emulsion is collected later and discarded.

Emulsion - The emulsion remaining after the free oil has been removed constituted the emulsion layer. The emulsion was broken using freeze/thaw cycles from -36 degrees to Room Temperature. The thawed emulsion was then centrifuged at >2500 RPM for 30 minutes to separate as much water as possible. After several cycles, the water content was minimal. The method of analysis of the oil for asphaltenes, saturates, aromatics and resins has been shown to be able to tolerate a small quantity of water without significantly affecting the results. Therefore, this method was deemed to be acceptable for the given application.

Hydrocarbon Group Analysis - The asphaltene content of the oil sample was determined by asphaltene precipitation according to ASTM Standard Method D 2007. The eluted maltenes are then blown dry using compressed air. The maltene components of the oil are then determined according to the methods as described in Jokuty et al., (1994, 1995). Only the non-volatile portions of the oil are analyzed.

Emulsion Formation and Long Term Standing

Emulsions were formed using the specified crude oil according to standard emulsion formation procedures outlined above, (Fingas, Fieldhouse et al., 1995b). A 1000 mL quantity of emulsion was then placed in a large beaker and allowed to stand in a 10 degree cold room for 3 months.

Layer Separation

Oil Layer - The oil layer was removed using a syringe with a large gauge needle. The oil was collected as close to the surface as possible, with care taken to avoid the emulsion below. If the emulsion was semi-solid, the beaker was be tipped to concentrate the oil at one end. Remaining oil on top of the emulsion was collected after and discarded.

Top 20% of Emulsion - An emulsion that has survived three months was found to have elasticity, giving the emulsion some rigidity. This enabled the collection of the emulsion using a spatula. The top layer of the emulsion was scooped up in small quantities covering the surface of the emulsion, and placed in a graduated cylinder until 200 mL had been collected.

Bottom 20% of Emulsion - The middle layer of emulsion between the top and bottom 20% was removed in the same manner as the top portion. A full 600 mL was not collected, as coalesced water on the bottom distorted the proportion. An estimation was made to leave approximately 200 mL of emulsion, which was collected for extraction.

Extraction of Oil from the Emulsion

Sampling - The extraction procedure was used on both of the emulsion layers from the experiment, as well as the oil layer. The sampling procedure collected approximately 10 mL of oil. The sample was homogenized by simple mixing/stirring, and an estimated amount of emulsion sampled to yield 10 to 15 mL of oil. In the case of the oil layer, 10 mL of mixed oil was sampled for extraction using a 10 mL disposable plastic syringe.

Extraction - The sample was put into a 500 mL glass separatory funnel. One-hundred mL of dichloromethane (DCM) and 50 mL of salt water (3.3% NaCl) was added to the sample. The separatory funnel was shaken for one minute and allowed to settle until most of the water and DCM had separated. The DCM layer was drained off to the turbid layer between the water and DCM phases, and collected into a 500 mL beaker. Care was taken to ensure that there were no water droplets in the DCM layer, as the dark colour makes it difficult to determine the presence of water. A 70/30 mixture of DCM and pentane, respectively, was added to the separatory funnel. This was again shaken for one minute and allowed to settle until most of the water and DCM phases had separated. Again the DCM layer was drained off into the 500 mL beaker. The rinsing of the sample with 50 mL aliquots of DCM/pentane was continued until the DCM layer was clear, usually between 4 and 6 rinse cycles, depending on the oil. When the DCM layer was clear and most of the DCM/pentane removed, 50 mL of benzene was added. The separatory funnel was shaken for one minute and allowed to settle. The water layer was then drained off, down to the turbid layer, into a separate beaker to be discarded. Two rinses of de-ionized water in the amount of 100 mL were performed, discarding the water from each rinse. The remaining benzene layer and the turbid layer containing water were both collected in the 500 mL beaker containing the rest of the effluent. The contents of the 500 mL collection beaker were roto-vapped down in a 100 mL boiling flask until the oil sample was obtained. The oil sample was then placed under a blow-down apparatus and blown with compressed air until remaining solvent was driven off.

Analysis - The asphaltene content of the oil sample was determined by asphaltene precipitation according to ASTM Standard Method D 2007. The maltenes

were then blown dry using compressed air. Weight difference was used in both instances to determine quantities. Only the non-volatile portions of the oil were analyzed.

Centrifuging Water Over Oil Procedure

Centrifuging - Salt water (2 mL 3.3% NaCl) was poured into a 15 mL disposable centrifuge tube. Oil (10 mL) was injected over the water from a 10 mL disposable plastic syringe. A total of six tubes were filled in this manner. The centrifuge tubes were then placed into a centrifuge and spun at 3300 RPM for 2.5 hours. The tubes were not moved from their places in the centrifuge as 2 mL of oil was removed from each tube by a syringe with a large gauge needle, keeping the tip as close to the surface as possible. The oil was collected for later analysis. Next, 6 mL of oil was removed from the centrifuge tube using the needle-tipped syringe, again without moving the tube, from the top of the remaining oil. The oil was sucked up slowly to reduce turbulence in the oil remaining in the tube. After all six tubes were sampled, the water under the remaining 2 mL of oil was removed by needle-tipped syringe and discarded. Then the oil and small layer of water were rinsed with two 5 mL volumes of de-ionized water. At this point, the contents of two centrifuge tubes were combined in a 25 mL beaker by washing with dichloromethane. The oil sample was blown down with compressed air until all solvent was driven off.

Analysis - The asphaltene content of the oil sample was determined by asphaltene precipitation according to ASTM Standard Method D 2007. The eluted maltenes were then blown dry using compressed air. Weight difference was used in both instances to determine quantities.

Side-by-side Standing Procedure

Emulsion Formation

Emulsions were formed using the specified crude oil according to standard emulsion formation procedures outlined above.

Side-by-side Standing

Emulsion (120 mL) was placed into a 125 mL wide-mouthed bottle. Teflon tape was wound around the threads of the bottle and upper rim. The mouth of the bottle was covered with a 10 cm x 10 cm square of 105 micron nylon mesh. A 60 mm ID Teflon collar was forcefully inserted over the mouth of the bottle, such that a firm seal is made between the mesh and the rim of the bottle, aided by Teflon tape. An aliquot of 120 mL of the crude oil was added into another 125 mL wide-mouthed bottle and used to form the emulsion. Teflon tape was wound around the threads and rim of the bottle, and covered with a 10 cm x 10 cm square of 105 micron nylon mesh. The first bottle was placed over the second and inserted into the Teflon collar, using the necessary force to complete the union.

The bottles in the collar were laid on their sides, and clamped into place with a C-clamp. Neoprene spacers were used to protect the bottles from the contact pressure of the C-clamp. The bottles remained horizontal for a period of one week in a 10 degree cold room.

Extraction of Oil from the Emulsion

Sampling - The extraction procedure was used on both the emulsion side of the experiment, as well as the source oil side. The procedure varied, depending on

the quantity of water expected to be contained in the emulsion. If 25 mL or less of oil was expected in the emulsion, the entire sample was extracted. If there was more oil present, then the sample was homogenized by simple mixing/stirring, and an estimated amount of emulsion sampled to yield 10 to 15 mL of oil. In the case of the oil layer, 10 mL of mixed oil was sampled for extraction using a 10 mL disposable plastic syringe.

Liquid/liquid Extraction - The sample was put into a 500 mL glass separatory funnel. Dichloromethane (DCM, 100 mL) was added to the sample as well as 50 mL of salt water (3.3% NaCl). The separatory funnel was shaken for one minute and allowed to settle until most of the water and DCM have separated. The DCM layer was drained off to the turbid layer between the water and DCM phases, and collected into a 500 mL beaker. Care was taken that there were no water droplets in the DCM layer, as the dark colour made it difficult to determine the presence of water. A 70/30 mixture of DCM and pentane, was added to the separatory funnel. This was again shaken for one minute and allowed to settle until most of the water and DCM phases had separated. Again the DCM layer was drained off into the 500 mL beaker. The rinsing of the sample with 50 mL aliquots of DCM/pentane was continued until the DCM layer was clear, between 4 and 6 rinse cycles, depending on the oil. When the DCM layer was clear and most of the DCM/pentane removed, 50 mL of benzene was added. The separatory funnel was shaken for one minute and allowed to settle. The water layer was then drained off, down to the turbid layer, into a separate beaker to be discarded. Two rinses of de-ionized water in the amount of 100 mL were performed, discarding the water from each rinse. The remaining benzene layer and the turbid layer containing water were both collected in the 500 mL beaker containing the rest of the effluent. The contents of the 500 mL collection beaker were roto-vapped down in a 100 mL boiling flask until the oil sample was obtained. The oil sample was then placed in a blow-down apparatus and blown with compressed air until remaining solvent was driven off.

Analysis - The asphaltene content of the oil sample was determined by asphaltene precipitation according to ASTM Standard Method D 2007. The eluted maltenes were then blown dry using compressed air. Weight difference was used in both instances to determine quantities. Note that all percentages reported are based on the non-volatile portion of the oil only, to establish a common point of reference.

Results and Discussion

Table 1 shows the results of all four series of experiments. Table 2 provides the summary results. The experiments entitled "one-week standing" were designed to determine if there was a separation of asphaltenes between the top oil layer and the lower emulsion layer. Table 1 shows that there is a concentration of both asphaltenes and resins in the emulsion layer. One particular experiment shows low concentration (-.04%), however this result is felt to be anomalous. It is interesting to note that both the resins and asphaltenes are concentrated in the emulsion layer. In terms of relative percent, asphaltenes are concentrated an average of 18% and resins an average of 10%. In the case where the emulsions were formed in the blender, perhaps leading to a more stable emulsion, asphaltenes are concentrated an average of 32% and resins an average of 1%. This appears to indicate that asphaltenes move downward to the emulsion layer, whereas a much less amount of resins migrate. Because the emulsion

Table 1 Experimental Results

Hydrocarbon Group Analysis Following One Week Standing

	Maltenes	Asphaltenes Total	%	Saturates	%	Aromatics	%	Resins 1	2	Total	%
Fresh Arabian Light Crude Oil											
Source Oil											
1	1.4259	0.0587	3.95	0.1769	46.59	0.1706	44.93	0.0278	0.0044	0.0322	8.48
2	1.3610	0.0530	3.75	0.2119	47.33	0.1994	44.54	0.0291	0.0073	0.0364	8.13
3	1.4326	0.0571	3.83	0.2209	47.34	0.2107	45.16	0.0284	0.0066	0.0350	7.50
Average			3.85		47.09		44.88				8.04
Std. Dev.			0.10		0.43		0.31				0.50
Arabian Light Oil Emulsion formed on the Rotary Agitator											
Free Oil Layer											
1	1.5345	0.0668	4.17	0.2241	47.11	0.2131	44.80	0.0289	0.0096	0.0385	8.09
2	1.5902	0.0635	3.84	0.2162	46.45	0.2104	45.21	0.0303	0.0085	0.0388	8.34
3	1.5530	0.0651	4.02	0.2178	47.20	0.2040	44.21	0.0295	0.0101	0.0396	8.58
Average			4.01		46.92		44.74				8.34
Std. Dev.			0.17		0.41		0.50				0.24
Free Oil Layer											
1	1.7085	0.0702	3.95	0.2277	46.95	0.2141	44.14	0.0344	0.0088	0.0432	8.91
2	1.7575	0.0732	4.00	0.2257	46.92	0.2144	44.57	0.0336	0.0073	0.0409	8.50
3	1.8284	0.0709	3.73	0.2245	46.79	0.2174	45.31	0.0299	0.0080	0.0379	7.90
4	1.5519	0.0645	3.99	0.2285	46.22	0.2261	45.73	0.0308	0.0090	0.0398	8.05
Average			3.92		46.72		44.94				8.34
Std. Dev.			0.12		0.34		0.71				0.46
Emulsion Layer											
1	1.1458	0.0453	3.80	0.2018	46.86	0.1874	43.52	0.0294	0.0120	0.0414	9.61
2	1.2642	0.0502	3.82	0.2320	48.78	0.1994	41.93	0.0329	0.0113	0.0442	9.29
3				0.2040	47.46	0.1879	43.72	0.0295	0.0084	0.0379	8.82
4				0.2198	48.04	0.2009	43.91	0.0296	0.0072	0.0368	8.04
Average			3.81		47.79		43.27				8.94
Std. Dev.			0.01		0.82		0.91				0.68
Emulsion											
1	1.6908	0.0917	5.14	0.2242	46.41	0.2169	44.90	0.0307	0.0113	0.0420	8.69
2	1.6979	0.0923	5.16	0.2207	45.70	0.2206	45.68	0.0316	0.0100	0.0416	8.61
3	0.9414	0.0514	5.18	0.2204	46.29	0.2118	44.49	0.0349	0.0090	0.0439	9.22
4				0.2209	45.91	0.2191	45.53	0.0312	0.0100	0.0412	8.56
Average			5.16		46.08		45.15				8.77
Std. Dev.			0.02		0.33		0.56				0.30
Arabian Light Oil Emulsion formed in the Blender				*Free Oil layer contaminated after sampling							
Emulsion											
1	1.5282	0.0789	4.91	0.2273	47.37	0.2126	44.31	0.0323	0.0076	0.0399	8.32
2	1.0931	0.0610	5.29	0.2020	47.44	0.1870	43.92	0.0300	0.0068	0.0368	8.64
3				0.2197	47.67	0.2080	45.13	0.0253	0.0079	0.0332	7.20
4				0.2076	46.87	0.1979	44.68	0.0318	0.0056	0.0374	8.44
Average			5.10		47.34		44.51				8.15
Std. Dev.			0.27		0.34		0.52				0.65

Long Term Standing (3 months)   Asphaltene content

Free Oil Layer					
1	1.7294	0.0644	3.59	Average	Std. Dev.
2	1.7857	0.0677	3.65	3.62	0.04
Top 20% of Emulsion					
1	1.7116	0.0803	4.48	Average	Std. Dev.
2	1.7604	0.08	4.34	4.41	0.10
Bottom 20% of Emulsion					
1	1.8953	0.14	6.83	Average	Std. Dev.
2	1.9559	0.14	6.60	6.71	0.16

Centrifuging Fresh Oil Over Salt Water

Arabian Light Crude Oil

Top 20% of Oil Layer					
1	1.9181	0.0915	4.55	Average	Std. Dev.
2	1.9521	0.0934	4.57	4.56	0.01
Bottom 20% of Oil Layer					
1	1.7630	0.1066	5.70	Average	Std. Dev.
2	2.3609	0.1443	5.76	5.65	0.14
3	2.2993	0.1335	5.49		

Side-by-side Standing for 1 week

Arabian Light Crude Oil

Emulsion Side					
1	1.9373	0.1053	5.16	Average	Std. Dev.
2	1.9038	0.1109	5.50	5.33	0.25
Oil Side					
1	2.0258	0.0952	4.49	Average	Std. Dev.
2	1.8806	0.0910	4.62	4.55	0.09

Transmountain Blend

Emulsion Side					
1	1.8456	0.1082	5.54	Average	Std. Dev.
2	1.8152	0.1008	5.26	5.40	0.20
Oil Side					
1	1.5350	0.0807	4.99	Average	Std. Dev.
2	1.7556	0.0972	5.25	5.12	0.18

Table 2   **Summary of Asphaltene and Resin Partitioning Studies**

Arabian Light crude and emulsion
Separation Following One-Week Standing

Location	Asphaltenes	Resins
Rotary shaker	**% absolute** change from starting oil	
Free oil layer	0.16	0.3
Free oil layer	0.07	0.3
Emulsion Layer	-0.04	0.9
Emulsion Layer	1.31	0.73
Blender formation		
Emulsion Layer	1.25	0.11
Long-term standing (3 months)		
Free oil layer	-0.23	
Top 20% of Emulsion	0.56	
Bottom 20% of Emulsion	2.86	
Centrifuging Oil over salt water		
Top 20% of oil layer	0.71	
Bottom 20% of oil layer	1.8	
Side-by-side experiment (1 week)		
Oil side	0.7	
Emulsion Side	1.48	
Transmountain blend oil		
Oil side	0	
Emulsion Side	0.85	

Separation Following One-Week Standing

Location	Asphaltenes	Resins
Rotary shaker	**% relative** change from starting oil	
Free oil layer	4.2	3.7
Free oil layer	1.8	3.7
Emulsion Layer	-1	11.2
Emulsion Layer	34	9.1
Blender formation		
Emulsion Layer	32.5	1.4
Long-term standing (3 months)		
Free oil layer	-6	
Top 20% of Emulsion	14.5	
Bottom 20% of Emulsion	74.3	
Centrifuging Oil over salt water		
Top 20% of oil layer	18.4	
Bottom 20% of oil layer	46.8	
Side-by-side experiment (1 week)		
Oil side	18.2	
Emulsion Side	38.4	
Transmountain blend oil		
Oil side	0	
Emulsion Side	18.7	

layer is underneath the oil layer in this case, at least part of this migration may be due to gravity separation of the heavier asphaltenes.

The second set of experiments involved the testing of an emulsion that had been standing for 3 months. Three layers were sampled, a free oil layer from the top, the top 20% (by height measurement) of the emulsion and the lower 20% of the emulsion. As Table 2 shows, the oil layer is depleted 0.23% in asphaltene content in absolute terms or 6% in relative terms. The top 20% is enriched by 15% in asphaltenes (relative percent) and the bottom by 74%. This indicates a strong partitioning of asphaltenes to the lower part of the emulsion system. Again, part of this may be due to gravitational settling of the asphaltenes.

A third experiment measured the asphaltene content of a salt water-emulsion-oil system in a centrifuge tube. This experiment was designed to measure whether asphaltenes would migrate to the oil-water interface. Gravity might be a factor, because, the centrifugal force should move the heavier asphaltenes to the bottom. In fact, the results as shown in Table 2, show that there is a greater concentration of asphaltenes at the oil-water interface (47% relative). This result shows that the asphaltenes will move to the oil-water interface and will be influenced by gravity.

A fourth series of experiments was conducted to examine how asphaltenes would migrate in the absence of a strong gravity effect. Two vessels were placed side-by-side, one with oil and the other with emulsion. Only a mesh separated the two materials. Sampling after one week showed an increase of 38% (relative) in asphaltenes in the emulsion formed from Arabian light crude and an increase of 17% in the emulsion formed from Transmountain blend oil.

These experiments show that asphaltenes migrate to the oil-water interface from the oil. This shows why an emulsion that sits for a period of time may become more viscous and more stable as time progress. During this time, asphaltenes are still migrating to the oil-water interface and thus rendering the emulsion more stable. The experiments show that migration still occurs after one or more weeks of contact. Furthermore, these experiments provide evidence that asphaltenes are the primary hydrocarbon group responsible for emulsion stability. Further work is necessary to determine if the resins will act in the same manner.

Conclusions

Asphaltenes are the primary agent responsible for the formation and stability of water-in-oil emulsions. These large compounds are interfacially active and behave like surfactants. Like surfactants, they can stabilize droplets of oil and water within each other, in this case water-in-oil. The role of resins may be important, however the experimental results in this paper, did not encompass resins to the same extent as asphaltenes.

Asphaltenes migrate to the oil-water interface from solution in oil. This process can continue over weeks. Experiments conducted as long as 3 months after emulsion formation, indicate that the asphaltene migration may still continue. This migration may explain the observation that many emulsions increase in stability and visco-elasticity after sitting for periods of time.

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